

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER

Mo-6379/LeA 33,294

U.S. APPLICATION NO. (If known, see 37 CFR 1.5

09/868792
To Be Assigned

INTERNATIONAL APPLICATION NO.

PCT/EP99/09915

INTERNATIONAL FILING DATE

December 14, 1999

PRIORITY DATE CLAIMED

December 24, 1998

TITLE OF INVENTION METHOD AND SYSTEM FOR PRODUCING SILANE

APPLICANT(S) FOR DO/EO/US BLOCK, Hans-Dieter; LEIMKUHLER, Hans-Joachim; MULLER, Dirk; SCHAFER, Johannes-Peter and RONGE, Georg

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Abstract

Form PTO 1449

U.S. APPLICATION NO. (if known, see 37 CFR 1.53)

To Be Assigned **09/868792**

INTERNATIONAL APPLICATION NO.

PCT/EP99/09915

ATTORNEY'S DOCKET NUMBER

Mo-6379/LeA 33,294

21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a) (2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO **\$1000.00**

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO **\$860.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$690.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) **\$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =**CALCULATIONS PTO USE ONLY**

\$ 860.00

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ 0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims:	14 -20 =	0	x \$18.00	\$ 0.00
Independent claims	2 -3 =	0	x \$80.00	\$ 0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$ 0.00

TOTAL OF ABOVE CALCULATIONS = \$ 860.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2. + \$ 0.00

SUBTOTAL = \$ 860.00

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$ 0.00

TOTAL NATIONAL FEE = \$ 860.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

\$ 40.00

TOTAL FEES ENCLOSED = \$ 900.00Amount to be
refunded: \$

charged: \$

- a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 900.00 to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

**00157**

PATENT TRADEMARK OFFICE

SIGNATURE

Diderico van Eyl
NAME

38,641
REGISTRATION NUMBER

09/868792

JC18 Rec'd PCT/PTO 2 1 JUN 2001

PATENT APPLICATION

Mo-6379

LeA 33,294

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
HANS-DIETER BLOCK ET AL) PCT/EP99/09915
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: METHOD AND SYSTEM FOR)
PRODUCING SILANE)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

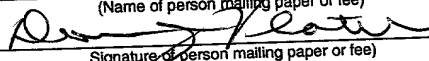
Prior to examination, please amend the application as follows:

"Express Mail" mailing label number ET146894943US
Date of Deposit June 21, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)



(Signature of person mailing paper or fee)

IN THE SPECIFICATION:

Please replace the title at page 1, line 1, with

--METHOD AND SYSTEM FOR PRODUCING SILANE--

IN THE CLAIMS:

Please replace the heading at page 15, line 1 with --WHAT IS CLAIMED IS:--

Please cancel Claims 1-14 and add Claims 15-28.

--15. A continuous process for the preparation of silane of formula SiH_4 by catalytic disproportionation of trichlorosilane of formula SiHCl_3 to form SiH_4 and silicon tetrachloride of formula SiCl_4 in a reactive/distillative reaction zone comprising

- (a) introducing SiHCl_3 into a reactive/distillative reaction zone comprising a catalyst bed of a catalytically active solid at a pressure of 1 to 50 bar to form a lower-boiling SiH_4 -containing product and a higher-boiling SiCl_4 -containing bottom product, and
- (b) removing the lower-boiling SiH_4 -containing product from the reactive/distillative reaction zone and condensing the SiH_4 -containing product in an intermediate condensation at a temperature in the range from -25°C to 50°C and further condensing any SiH_4 -containing product that is not condensed in the intermediate condensation in an overhead condenser from which the SiH_4 -containing product is discharged as final product.

16. A process according to Claim 15 wherein the pressure in the catalyst bed is from 1 to 10 bar.

17. A process according to Claim 15 wherein the intermediate condensation is carried out at a temperature in the range between -5°C and 40°C .

18. A process according to Claim 17 wherein the product mixture obtained in the overhead condenser is separated at a pressure higher than the pressure employed in the intermediate condensation.

19. A process according to Claim 17 wherein all or part of the chlorosilane is returned to the reactive/distillative reaction zone.

20. An installation for the continuous preparation of silane of formula SiH_4 by catalytic disproportionation of trichlorosilane of formula SiHCl_3 to form SiH_4 and silicon tetrachloride of formula SiCl_4 in a reaction column having

- (1) a reactive/distillative reaction zone comprising a catalyst bed made of solid bodies of catalytically active solid and through which the disproportionation products and trichlorosilane can flow,
- (2) an inlet for introducing SiHCl_3 into the reaction zone,
- (3) an overhead condenser connected to the reaction column for condensing the SiH_4 -containing product that is formed and having an outlet for condensed SiH_4 at the overhead condenser,
- (4) at least one intermediate condenser arranged between the reactive/distillative reaction zone and the overhead condenser, wherein the intermediate condenser is operated at a temperature in the range from -25°C to 50°C , and
- (5) an outflow for SiCl_4 obtained as bottom product, for carrying out the process according to Claim 1.

21. An installation according to Claim 20 wherein a temperature in the intermediate condenser is set in the range from -5°C to 40°C .

22. An installation according to Claim 20 wherein the intermediate condenser is arranged above the catalyst bed.

23. An installation according to Claim 20 wherein a rectifying section for increasing the SiH_4 concentration in the product mixture is arranged downstream of the intermediate condenser in the direction of flow of the lower-boiling product mixture coming from the intermediate condenser.

24. An installation according to Claim 20 wherein a separation column for separating SiH_4 -containing product fractions from higher-boiling chlorosilane components is arranged downstream of the intermediate condenser in the direction of flow of the lower-boiling product mixture coming from the intermediate condenser.

25. An installation according to Claim 24 wherein the separation column is arranged downstream of the rectifying section.

26. An installation according to Claim 25 wherein a condenser is arranged between rectifying section and the separation column.

27. An installation according to Claim 24 wherein the separation column is operated at a pressure higher than the pressure in the intermediate condenser and the product that is conducted to the separation column is compressed.

28. An installation according to Claim 24 wherein a branch line that opens into the reactive/distillative reaction zone of the reaction column is connected to the bottom outlet of the separation column.--

IN THE ABSTRACT:

Please add an Abstract as new page 17 to read as follows:

--LeA 33 294-Foreign Countries

- 17 -

METHOD AND SYSTEM FOR PRODUCING SILANE

ABSTRACT OF THE DISCLOSURE

This invention relates to a continuous process for the preparation of silane by catalytic disproportionation of trichlorosilane in a reactive/distillative reaction zone comprising a catalyst bed of catalytically active solid.--

REMARKS

Applicants hereby offer preliminary amendments to the present application to place the application in better form for allowance.

Applicants have canceled Claims 1-14 in favor of replacement Claims 15-28 to correct certain informalities (including multiple dependencies) and to clarify the intended meaning of the claims. Applicants respectfully submit that the claims are fully supported in the specification.

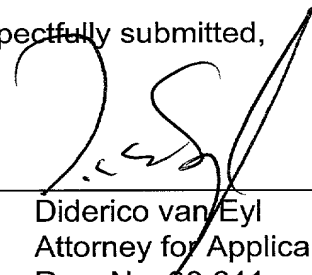
Applicants have amended the specification to change the title to correspond to the English version of the title appearing on the International Application and to capitalize all letters in the title. Applicants submit that these amendments serve only to clarify their application and do not alter the scope of their disclosure.

Applicants have added an Abstract that summarizes the subject matter of their invention. A copy of the new Abstract is separately attached.

In view of the preceding amendments and remarks, allowance of the claims is respectfully requested.

Respectfully submitted,

By


Diderico van Eyl
Attorney for Applicants
Reg. No. 38,641

Bayer Corporation
100 Bayer Road
Pittsburgh, Pennsylvania 15205-9741
(412) 777-8341
FACSIMILE PHONE NUMBER:
(412) 777-8363

s:/sr/relh0325

ANNOTATED VERSION OF AMENDMENTS

IN THE SPECIFICATION:

The title at page 1, line 1, has been changed from "Process and installation for the preparation of silane" to

--METHOD AND SYSTEM FOR PRODUCING SILANE--

IN THE CLAIMS:

The heading for the claims at page 15, line 1 has been changed from "Patent Claims" to --WHAT IS CLAIMED IS:--

Claims 1-14 have been canceled in favor of replacement Claims 15-28.

--15. A continuous process for the preparation of silane of formula SiH_4 by catalytic disproportionation of trichlorosilane of formula SiHCl_3 to form SiH_4 and silicon tetrachloride of formula SiCl_4 in a reactive/distillative reaction zone comprising

- (a) introducing SiHCl_3 into a reactive/distillative reaction zone comprising a catalyst bed of a catalytically active solid at a pressure of 1 to 50 bar to form a lower-boiling SiH_4 -containing product and a higher-boiling SiCl_4 -containing bottom product, and
- (b) removing the lower-boiling SiH_4 -containing product from the reactive/distillative reaction zone and condensing the SiH_4 -containing product in an intermediate condensation at a temperature in the range from -25°C to 50°C and further condensing any SiH_4 -containing product that is not condensed in the intermediate condensation in an overhead condenser from which the SiH_4 -containing product is discharged as final product.

16. A process according to Claim 15 wherein the pressure in the catalyst bed is from 1 to 10 bar.

17. A process according to Claim 15 wherein the intermediate condensation is carried out at a temperature in the range between -5°C and 40°C .

18. A process according to Claim 17 wherein the product mixture obtained in the overhead condenser is separated at a pressure higher than the pressure employed in the intermediate condensation.

19. A process according to Claim 17 wherein all or part of the chlorosilane is returned to the reactive/distillative reaction zone.

20. An installation for the continuous preparation of silane of formula SiH_4 by catalytic disproportionation of trichlorosilane of formula SiHCl_3 to form SiH_4 and silicon tetrachloride of formula SiCl_4 in a reaction column having

- (1) a reactive/distillative reaction zone comprising a catalyst bed made of solid bodies of catalytically active solid and through which the disproportionation products and trichlorosilane can flow,
- (2) an inlet for introducing SiHCl_3 into the reaction zone,
- (3) an overhead condenser connected to the reaction column for condensing the SiH_4 -containing product that is formed and having an outlet for condensed SiH_4 at the overhead condenser,
- (4) at least one intermediate condenser arranged between the reactive/distillative reaction zone and the overhead condenser, wherein the intermediate condenser is operated at a temperature in the range from -25°C to 50°C , and
- (5) an outflow for SiCl_4 obtained as bottom product, for carrying out the process according to Claim 1.

21. An installation according to Claim 20 wherein a temperature in the intermediate condenser is set in the range from -5°C to 40°C .

22. An installation according to Claim 20 wherein the intermediate condenser is arranged above the catalyst bed.

23. An installation according to Claim 20 wherein a rectifying section for increasing the SiH_4 concentration in the product mixture is arranged downstream of the intermediate condenser in the direction of flow of the lower-boiling product mixture coming from the intermediate condenser.

24. An installation according to Claim 20 wherein a separation column for

separating SiH₄-containing product fractions from higher-boiling chlorosilane components is arranged downstream of the intermediate condenser in the direction of flow of the lower-boiling product mixture coming from the intermediate condenser.

25. An installation according to Claim 24 wherein the separation column is arranged downstream of the rectifying section.

26. An installation according to Claim 25 wherein a condenser is arranged between rectifying section and the separation column.

27. An installation according to Claim 24 wherein the separation column is operated at a pressure higher than the pressure in the intermediate condenser and the product that is conducted to the separation column is compressed.

28. An installation according to Claim 24 wherein a branch line that opens into the reactive/distillative reaction zone of the reaction column is connected to the bottom outlet of the separation column.--

IN THE ABSTRACT:

An Abstract has been added as new page 17 as follows:

--LeA 33 294-Foreign Countries

- 17 -

METHOD AND SYSTEM FOR PRODUCING SILANE

ABSTRACT OF THE DISCLOSURE

This invention relates to a continuous process for the preparation of silane by catalytic disproportionation of trichlorosilane in a reactive/distillative reaction zone comprising a catalyst bed of catalytically active solid.--

METHOD AND SYSTEM FOR PRODUCING SILANE

ABSTRACT OF THE DISCLOSURE

This invention relates to a continuous process for the preparation of silane by catalytic disproportionation of trichlorosilane in a reactive/distillative reaction zone comprising a catalyst bed of catalytically active solid.

1. A continuous process for the preparation of silane by catalytic disproportionation of trichlorosilane in a reactive/distillative reaction zone comprising a catalyst bed of catalytically active solid.

3/PR75

- 1 -

Process and installation for the preparation of silane

The present invention relates to a continuous process for the preparation of silane SiH_4 by catalytic disproportionation of trichlorosilane SiHCl_3 to form SiH_4 and silicon tetrachloride SiCl_4 . The invention further relates to an installation for carrying out the process.

SiH_4 is a very suitable starting material from which, optionally after further purification, very pure silicon of semiconductor grade can be deposited by thermal decomposition. There is a strongly increasing demand for ultrapure silicon and thus for pure silane which is recognized and utilized more and more as a very suitable source of ultrapure silicon.

From the silane preparation processes described in the literature, the trichlorosilane disproportionation is economically advantageous. The use of amines, especially tertiary amines and hydrochlorides thereof and quaternary ammonium chlorides, both in liquid form (DE 3 500 318) and in solid form, e.g. bound to solid supports, as catalysts is known to accelerate the disproportionation of the trichlorosilane in an economically advantageous manner. The use of amines bound to solid supports (US 4 701 430, US 5 026 533, DE 3 500 318, DE 3 311 650) is therefore preferred because the contamination of the reacting silane/chlorosilane gas/liquid phase with amines can be avoided in this way.

A disadvantage of the liquid catalysts selected in some other existing processes is that they are discharged from the reaction section slowly over time, because they can never be separated completely from the reaction products. The entrained amounts of catalyst give rise to problems in downstream process steps or, in a circulation system, also in upstream process steps, because they can accumulate at certain points in the system where they can catalyze undesired reactions, for example. In addition, it is not possible to achieve a very uniform distribution of a liquid catalyst in the column, rather the catalyst will locally concentrate owing to its specific vapor pressure. This

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Donna J. Yeatch

(Name of person mailing paper or fee)

Signature of person mailing paper or fee

problem is in no way solved, but at best alleviated, by the use of two catalysts having different boiling points as proposed in DE 3 500 318.

Attempts have already been made to conduct the disproportionation, which, according to the prior art, is a multistep process, for example a two-step process, in one step applying the principle of reactive distillation. Reactive distillation is characterized by a combination of reaction and distillative separation in a single apparatus, in particular a column. The continuous distillative removal of the lowest-boiling component respectively in each element of space ensures that an optimum difference between the equilibrium state and the actual content of lower-boiling components or lowest-boiling component is always maintained, resulting in a maximum reaction rate (JP-01 317 114).

DE 2 507 864 discloses another process for the preparation of silane which comprises introducing trichlorosilane into a bed of an anion exchange resin which is insoluble in the reaction medium and contains tertiary amino or quaternary ammonium groups bonded to a carbon atom, maintaining the resin bed at a temperature sufficient to cause trichlorosilane to be disproportionated to form products which rise in the bed, and silicon tetrachloride which condenses and flows to the column bottom, and maintaining the top part of the bed at a temperature above the boiling point of silane and below the boiling point of monochlorosilane, and recovering from the bed silane which is virtually chlorosilane-free.

This process is distinguished from the other known processes by the following features:

- (1) it can be carried out in a single apparatus, i.e. the desired, enriched products silane and silicon tetrachloride can be taken off at different points of the same apparatus, and therefore requires a comparatively low expenditure in terms of apparatus and energy;

(2) it makes it possible to obtain the products silane (in concentrations of between 96 to 98% of SiH_4) and silicon tetrachloride (in concentrations of e.g. between 70 to 80% of SiCl_4) in comparatively high concentration without the need for further auxiliary units;

5

(3) owing to the solid insoluble catalyst (hereinafter called catalytically active solid), the introduction of impurities from the catalyst into the reaction mixture is minimized, the separation of the catalyst is significantly easier than in the case of the liquid soluble catalysts, and the accumulation of volatile, liquid catalysts in certain column parts is strictly avoided; and

10

(4) the amount of energy required for the separation of the silanes or chlorosilanes formed in the individual equilibrium stages of the disproportionation is minimized by the principle of reactive rectification.

15

A grave disadvantage of this process described in DE 2 507 864 is that the amount of energy utilized for the separation of the silanes or chlorosilanes has to be completely removed at a very low temperature level matched to the condensation temperatures. In fact, DE 2 507 864 requires that the temperature at the top of the column be below the condensation temperature of monochlorosilane SiH_3Cl and that the temperature in the trichlorosilane SiHCl_3 feed zone be such that trichlorosilane can be evaporated. Thus, the energy required for evaporating the various chlorosilanes and the silane in the individual sections of the column is actually removed at a temperature below the condensation temperature of the monochlorosilane, i.e. from below -50°C to -120°C . However, heat removal at a low temperature level is known to be costly and requires additional energy, and indeed the lower the temperature to be set for the coolant, the higher the amount of additional energy required.

20

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It is an object of the invention to provide a continuous process and an installation for the preparation of silane by catalytic disproportionation of trichlorosilane to form silane and silicon tetrachloride in which the disproportionation proceeds in a

reactive/distillative manner over catalytically active solids, silane and silicon - tetrachloride are recovered in comparatively high concentration, and the disproportionated products are separated and condensed with minimal expenditure. The heat is to be removed essentially at a temperature level at which the coolant can be used which has a temperature that can be achieved quite easily, and the apparatus and energy required for refrigeration to remove the heat for condensing the products is to be reduced.

A continuous process for the preparation of silane SiH_4 by catalytic disproportionation of trichlorosilane SiHCl_3 to form SiH_4 and silicon tetrachloride SiCl_4 in a reactive/distillative reaction zone comprising a catalyst bed of catalytically active solid, into which SiHCl_3 is introduced and from which lower-boiling SiH_4 -containing product formed in the catalyst bed is taken off and condensed in an overhead condenser and discharged as final product, and in which SiCl_4 is formed as higher-boiling bottom product, is provided which is characterized in that the lower-boiling product mixture, which has formed in the catalyst bed at a pressure of 1 to 50 bar, is subjected to an intermediate condensation at a temperature in the range from -25°C to 50°C , and the SiH_4 -containing product mixture which is not condensed in the intermediate condensation is condensed in the overhead condenser.

Suitable catalytically active solids are known and also described in DE 2 507 864. For example, they are solids which contain, on a framework of divinylbenzene-crosslinked polystyrene, amino or alkyleneamino groups such as dimethylamino, diethylamino, ethylmethylamino, di-n-propylamino, di-i-propylamino, di-2-chloroethylamino, di-2-chloropropylamino groups and hydrochlorides thereof, or trialkylammonium groups formed therefrom by methylation, ethylation, propylation, butylation, hydroxyethylation or benzylation, with chloride counterion. In the case of quaternary ammonium salts or protonated ammonium salts it is of course also possible to introduce into the process according to invention catalytically active solids containing other anions, e.g. hydroxide, sulfate, hydrogensulfate, bicarbonate

etc., in the course of time, these are, however, inevitably converted into the chloride form under the reaction conditions, which also applies to organic hydroxyl groups.

5 Other suitable solids are those composed of a polyacrylic acid framework, especially a polyacrylamide framework, to which e.g. trialkylbenzylammonium is attached via an alkyl group.

10 Another group of catalytically active solids which is suitable for the process according to the invention are those which have sulfonate groups attached to a divinylbenzene-crosslinked polystyrene framework, balanced with tertiary or quaternary ammonium groups as cations.

15 Macroporous or mesoporous exchange resins are usually more suitable than gel resins. Other suitable catalytically active solids are those which carry organic amino groups of the abovementioned type, e.g. those which have a 3-siloxypropyl-dimethylamino group, attached to a solid inorganic framework such as silica or zeolite (US 4 701 430). Suitable catalytically active solids are usually employed in the form of beads.

20 A number of suitable activation and pretreatment methods for these catalysts are described in the literature.

25 In a preferred embodiment of the process according to the invention, the SiH_4 -containing product mixture is separated from the higher-boiling chlorosilanes present in the mixture prior to condensation of the final SiH_4 product so as to increase the SiH_4 concentration. The separation is preferably conducted at a pressure which is higher than that employed in the intermediate condensation, so that the concentration of the SiH_4 can be achieved at a higher temperature level and thus less product is to be condensed at a higher SiH_4 concentration. Chlorosilane obtained in the separation
30 is conveniently returned to the reactive/distillative reaction zone.

The invention and further embodiments thereof are illustrated below with reference to installations for carrying out the process and corresponding examples. Specifically, in the drawing:

5 Figure 1 shows an installation for the production of silane comprising a reactive/distillative reaction zone, an intermediate condenser, integrated rectifying section and, downstream of the rectifying section, an external overhead condenser for condensing silane;

10 Figure 2 shows an installation for the production of silane comprising a reactive/distillative reaction zone, an intermediate condenser, integrated rectifying section and, downstream of the rectifying section, an external condenser, a separation column downstream of the latter, and an overhead condenser for condensing silane which is connected to the separation column.

15 Figure 3 shows an embodiment with external reactors.

20 Figure 1 shows a flow chart for an installation for the continuous production of silane SiH_4 which comprises an essentially vertical reaction column 1 having a reactive/distillative reaction zone 2 for the catalytic disproportionation of trichlorosilane SiHCl_3 . The disproportionation in the reaction zone 2 is conducted in a catalyst bed 2' which is made of a randomly packed layer of solid bodies of catalytically active solid and through which the disproportionation products can flow.

25 Instead of a randomly packed layer, the reaction zone may also contain catalyst bodies in a structured packing. Catalytically active solids are preferably those described in DE 2 507 864, as mentioned above.

30 The SiHCl_3 is introduced into the reaction column 1 via an inlet 3 which opens into the column at an appropriate point. In the reaction zone 2, disproportionation of

SiHCl_3 yields an SiH_4 -containing product mixture which ascends in the reaction zone and an SiCl_4 -containing condensate which descends in the reaction zone.

In the reaction column 1, the SiCl_4 -containing condensate exiting from the reaction zone is introduced into a distillative stripping section 4 which is arranged below the reactive/distillative reaction zone 2. From a bottom evaporator 5, arranged below the stripping section, silicon tetrachloride SiCl_4 is discharged as bottom product via an outflow 13. The amount of heat required for the disproportionation of SiHCl_3 is introduced into the reaction column by means of the heat exchanger 5.

Above the reaction zone, an intermediate condenser 6 is provided for the SiH_4 -containing product mixture ascending in the reaction zone 2. In this condenser, the SiH_4 concentration in the product mixture is increased by partial condensation of higher-boiling components at a temperature between -25°C and 50°C , preferably between -5°C and 40°C . The heat of condensation is dissipated by a coolant flowing through the intermediate condenser 6. The lower-boiling product fractions which are not condensed in the intermediate condenser 6 are introduced into a rectifying section 7 which is arranged downstream of the intermediate condenser in the direction of flow of the ascending product fractions, and further concentrated. In the embodiment of Figure 1, the rectifying section 7 is inserted above the intermediate condenser 6 and integrated into the reaction column 1. Alternatively, the rectifying section can be arranged outside the reaction column. The product mixture from the rectifying section 7 is finally taken off at the top of the reaction column via an outlet 8 and introduced into an overhead condenser 9 in which it is condensed and discharged in liquid form, as final SiH_4 product obtained, via an SiH_4 product line 10. Part of the recovered SiH_4 is returned to the top of the reaction column 1 via a branch line 11. The branch line 11 opens into the column above the rectifying section 7.

Residual inert gas fractions obtained in the overhead condenser 9 during SiH_4 condensation are discharged from the overhead condenser via an inert gas line 12.

According to the invention, in the embodiment of Figure 1, condensation of the product taken off at the top of the reaction column 1 in the overhead condenser 9 produces silane in a concentration of >70 %, preferably >90 %, particularly preferably >98 %. Following disproportionation of SiHCl_3 in the reactive/distillative reaction zone 2, the lower-boiling SiH_4 -containing product which is ascending from the reaction zone to the top of the reaction column 1 is subjected to an intermediate condensation. Instead of one intermediate condenser, as described in the embodiment above, a plurality of intermediate condensers can be inserted. The intermediate condenser(s) 6 operate at temperatures at which the removal of the heat of condensation by means of a coolant is still possible between -25°C and 50°C , preferably between -5°C and 40°C , so that only a considerably smaller, uncondensed fraction of the SiH_4 -containing product mixture has to be transferred to a rectifying section 7 equipped with conventional distillation internals such as trays and packings, and only the gas fraction exiting the rectifying section has to be condensed in the overhead condenser 9 at very low temperatures in a final step.

Moreover, the rectifying section 7 including its associated overhead condenser 9 can also be arranged externally outside the reaction column 1.

With conventional pressures of 1 to 50 bar, preferably 1 to 10 bar, and the desired purities of the silane product, the overhead condenser 9 has to be operated below the condensation temperatures of $<-40^\circ\text{C}$, in most cases even below $<-60^\circ\text{C}$. By installing purely distillative separation sections upstream of the condensation of the final silane product and arranging a distillative stripping section 4 above the bottom evaporator 5, the energy introduced is used several times, i.e. (1) for purifying and concentrating the silane in the rectifying section 7, (2) for continuous distillative removal of those intermediates or products which are lower-boiling under the respective local conditions in the apparatus and thus for increasing the reaction rate in the reactive/distillative reaction zone 2, and (3) for purifying the SiCl_4 in the lower part of the reaction column. A further advantage compared to the process disclosed in DE 2 507 864 results from the distillative stripping section 4 and the resulting

possibility of purifying the SiCl_4 discharged at the bottom, because a downstream SiCl_4 purification column can be omitted, thus reducing the energy required for this process step.

5 Another embodiment is shown in Figure 2. In this embodiment, the construction of the reaction column 1a is similar to the design of the reaction column 1 of Figure 1. Therefore, all equipment parts designed in analogy to the parts of Figures 1 and 2 are given the same reference symbols, but are represented with the added index "a" to distinguish them.

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In the embodiment of Figure 2, the separation column 14 is arranged downstream of a condenser 9a which is located between rectifying section 7a and separation column 14. In the condenser 9a, all or part of the uncondensed SiH_4 -containing product mixture exiting the rectifying section 7a via the outlet 8a is condensed prior to entering the separation column 14, so that a product mixture which is more concentrated in SiH_4 is introduced into the separation column 14. Part of the condensate obtained in the condenser 9a is returned, via a branch line 11a, to the reaction column 1a above its rectifying section 7a. The remaining part of the condensate is compressed by means of a liquid pump 15 and transferred to the separation column 14 via a pressure line 16. If only part of the product mixture exiting the rectifying section 7a is condensed in the condenser 9a, the remaining part is sucked off via an outlet 12a by means of a compressor 17, compressed and introduced into the separation column 14 via a pressure line 16'. Alternatively, the stream 12a can be transferred to a workup step.

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An outlet 18 leads from the top of the separation column 14 to an overhead condenser 19 from which the condensed silane obtained is discharged in an SiH_4 product line 20. Part of the liquid silane is returned to the separation column 14 in a branch line 21. Inert gases obtained in the overhead condenser are discharged via an inert gas line 22.

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The bottom product of the separation column 14 is discharged from the bottom 23 of the separation column via a bottom outlet 24. Part of the bottom product flows back into the reaction column 1a via the branch line 25, another part is returned to the bottom zone of the separation column 14 via a return line 26 after evaporation in the heat exchanger 27, another part can be bled off (28) completely from the plant in order to remove impurities.

In the embodiment of Figure 2, a liquid or gaseous overhead product having a lower silane purity of between 25 % to 90 % is produced by reducing the reflux compared to the embodiment of Figure 1 and complete or partial condensation in the condenser 9a so as to increase the condensation temperature in the overhead condenser 9a and to reduce further the condensation energy which has to be removed at a very low temperature. This overhead product is then purified further by separation in the downstream separation column 14, where the same pressure or preferably a higher pressure than in the reaction column 1a, preferably 15 bar to 100 bar, is set, so that the separation column 14 operates at higher temperatures than the reaction column 1a, based on the same composition. In this variant too, the bottom product of the separate separation column 14 may contain large proportions of trichlorosilane, dichlorosilane and monochlorosilane, depending on the operating conditions selected. All or part of the bottom product is returned to the reaction column 1a via the branch line 25 connected to the outlet 24. If necessary, impurities can be removed (28) from the system by bleeding off a part-stream.

The feed(s) introduced into the reaction column via the inlets 3, 3a and 25, if desired after preliminary reaction in a preliminary reactor, are introduced into the stripping section 4, 4a, or between reactive/distillative reaction zones 2, 2a and stripping section, or into the reactive-distillative reaction zone, or into the overhead condenser 6, 6a, depending on the respective composition.

The process according to the invention is conducted at pressures from 1 to 50 bar, preferably 1 to 10 bar, particularly preferably 2.8 to 5 bar, in the reactive/distillative

reaction zone using catalytically active solids. The temperatures in the system are varied by means of the pressures. The temperatures in that part of the reactive/distillative reaction section in which the disproportionation takes place are between 30°C and 180°C, preferably between 50°C and 110°C. The temperature
5 which is to be set in each case depends on the range in which the catalytically active solids are stable.

A disadvantage of the previously described processes for the distillative separation of pure silane with concomitant reaction is the large amount of heat which has to be
10 removed at the condensation temperature of the silane at a given pressure, i.e. for example at -50°C to -120°C. As mentioned above, condensation at these temperatures is economically very unfavorable. As the amount of heat which has to be removed during operation without intermediate condenser is of the same order as the amount of heat introduced at the bottom of the reaction column, the heat removal
15 costs should generally be considerably higher than the heat introduction costs. This is largely avoided by the intermediate condensation according to the invention. For example, depending on the system pressure, 60% to 97% of the heat of condensation can be removed when using a coolant having a temperature of 25°C for the intermediate condensation to cool down the gas stream exiting above the intermediate
20 condenser(s) to 40°C, so that only 3% to 40% of the heat of condensation have to be removed at the condensation temperature of the silane. Nevertheless, purification of the silane to give an SiH_4 content of preferably more than 90%, particularly preferably more than 98%, is possible above the intermediate condenser in a separation column placed directly above the intermediate condenser and/or in a
25 separate separation column, the condenser for condensing silane at the head of the separation column being operated at a coolant temperature below the condensation temperature of the silane.

Owing to the intermediate condensation, the conditions in the reaction areas in the
30 reactive/distillative reaction zone remain essentially unchanged compared to a reaction column without intermediate condenser, so that intermediates and products

formed can still be separated effectively by distillation after their formation. It is only above the intermediate condenser that the vapor and liquid streams are significantly reduced compared to the rest of the system. However, they are sufficient to ensure that the silane which is present in small amounts compared to the bottom product of the reaction column, SiCl_4 , and whose boiling point differs considerably from the remaining components, is concentrated in a separation column placed on top or in a separate separation column, achieving purities of >50 %, particularly preferably >98 %.

Preferred internals used in the reaction columns of the installation according to the invention are those which ensure an intensive mass transfer between gas phase and liquid phase and simultaneously allow an intensive contact with the solid catalyst. Owing to the combination of mass transfer and reaction, a sufficient distance from the respective reaction equilibrium is ensured in the reactive/distillative reaction zone by rapid separation of products formed, so that the reaction always proceeds with a high reaction rate. Examples of such column internals are trays, structured or random packings for introducing heterogeneous catalysts, as described, for example, in the following publications: EP 670 178, EP 461 855, US 5 026 459, US 4 536 373, WO 94/08 681, WO 94/08 682, WO 94/08 679, EP 470 655, WO 97/26 971, US 5 308 451, EP 755 706, EP 781 829, EP 428 265, EP 448 884, EP 640 385, EP 631 813, WO 90/02 603, WO 97/24 174, EP 665 041, EP 458 472, EP 476 938 and German Utility Model 298 07 007.3. Alternatively, the solid catalyst can be spread on distillation trays as such or in agglomerated form. When carrying out the process, residence time, catalyst volume and distillative separation effect in the reaction zone are matched to reaction kinetics and mass transfer kinetics, the parameter optimum depending strongly on the boundary conditions, such as the catalyst selected, the system of substances and the pressure and temperature conditions selected.

Alternatively, the catalyst can be introduced into external, optionally thermostatted reactors, alternating between transferring the liquid phase from the reaction column into the reactor and from the reactor back to the column for separation of substances.

In this case, however, it is disadvantageous that products formed generally cannot be separated by distillation as rapidly after their formation as in the case of the abovementioned trays, structured packings and random packings. Decoupling of different temperatures in the column and in external reactions can be achieved by
5 thermostating the material streams between the column and the reactors.

Figure 3 shows the distillative/reactive reaction zone 2; 2a of Figures 1 and 2 for the embodiment having external reactors. The liquid mixture flowing out of a distillative section 29 enters, optionally via heat recovery unit and thermostating unit 31, a
10 reactor 32 operated in downward or upward flow mode, and is passed on into the subsequent distillative section. The sequence "distillative section/thermostating unit/reactor" can be repeated on top of one another any number of times.

According to the invention, the disproportionation which is taking place in the
15 reaction zone of the reaction columns is supplemented by a purely distillative separation and purification of the silane- or silicon tetrachloride-containing products to be discharged at the top and at the bottom of the reaction columns. The distillative separation is carried out by means of conventional internals for pure distillation such as trays, structured packings and random packings. For the exiting higher-boiling
20 SiCl_4 component it is convenient to produce a substantially concentrated silicon tetrachloride bottom product containing more than 70% of SiCl_4 , preferably more than 95% of SiCl_4 , particularly preferably more than 99% of SiCl_4 , by purely distillative separation below the reactive/distillative reaction zone in the bottom part of the reaction column, and to take off this product at the bottom of the reaction
25 column.

List of reference symbols

	Reaction column	1, 1a
	Reactive/distillative reaction zone	2, 2a
5	Catalyst bed	2', 2a'
	SiHCl ₃ inlet	3, 3a
	Distillative stripping section	4, 4a
	Bottom evaporator	5, 5a
	Intermediate condenser	6, 6a
10	Intermediate condenser	7, 7a
	Vapor outlet	8, 8a
	Overhead condenser	9, 9a
	SiH ₄ product line	10, 10a
	Branch line	11, 11a
15	Inert gas line	12, 12a
	SiCl ₄ outflow	13, 13a
	Separation column	14
	Liquid pump	15
	Pressure line	16
20	Compressor	17
	Outlet	18
	Overhead condenser	19
	SiH ₄ product line	20
	Branch line	21
25	Inert gas line	22
	Bottom	23
	Bottom outlet	24
	Branch line	25
	Return line	26
30	Heat exchanger	27
	Bleed-off	28
	Distillation section	29
	Heat recovery unit	30
	Thermostatting unit/heat exchanger	31
35	Reactor	32

Patent Claims

1. Continuous process for the preparation of silane SiH_4 by catalytic disproportionation of trichlorosilane SiHCl_3 to form SiH_4 and silicon tetrachloride SiCl_4 in a reactive/distillative reaction zone comprising a catalyst bed of catalytically active solid, into which SiHCl_3 is introduced and from which lower-boiling SiH_4 -containing product formed in the catalyst bed is taken off and condensed in an overhead condenser and discharged as final product, and in which SiCl_4 is formed as higher-boiling bottom product, characterized in that the lower-boiling product mixture, which has formed in the catalyst bed at a pressure of 1 to 50 bar, is subjected to an intermediate condensation at a temperature in the range from -25°C to 50°C , and the SiH_4 -containing product mixture which is not condensed in the intermediate condensation is condensed in the overhead condenser.
2. Process according to Claim 1, characterized in that the pressure in the catalyst bed is from 1 to 10 bar.
3. Process according to Claim 1, characterized in that the intermediate condensation is carried out at a temperature in the range between -5°C and 40°C .
4. Process according to Claim 3, characterized in that the product mixture obtained in the overhead condenser is separated at a pressure which is higher than that employed in the intermediate condensation.
5. Process according to Claim 3 or 4, characterized in that all or part of the chlorosilane is returned to the reactive/distillative reaction zone.
6. Installation for the continuous preparation of silane SiH_4 by catalytic disproportionation of trichlorosilane SiHCl_3 to form SiH_4 and silicon tetra-

- chloride SiCl_4 in a reaction column (1, 1a) having a reactive/distillative reaction zone (2, 2a) which comprises a catalyst bed (2', 2a') which is made of solid bodies of catalytically active solid and through which the disproportionation products and trichlorosilane can flow, an inlet (3, 3a) for introducing SiHCl_3 into the reaction zone, and an overhead condenser (9, 9a) connected to the reaction column for condensing SiH_4 -containing product formed and an outlet for condensed SiH_4 at the overhead condenser (10, 10a), and an outflow (13, 13a) at the reaction column for SiCl_4 which is obtained as bottom product, for carrying out the process according to Claim 1, characterized in that at least one intermediate condenser (6, 6a) is arranged between the reactive/distillative reaction zone (2, 2a) and the overhead condenser (9, 9a), the intermediate condenser being operated at a temperature in the range from -25°C to 50°C .
7. Installation according to Claim 6, characterized in that a temperature in the range from -5°C to 40°C is set in the intermediate condenser (6, 6a).
8. Installation according to Claim 6 or 7, characterized in that the intermediate condenser (6, 6a) is arranged above the catalyst bed (2', 2a').
9. Installation according to one of Claims 6, 7 or 8, characterized in that a rectifying section (7, 7a) for increasing the SiH_4 concentration in the product mixture is arranged downstream of the intermediate condenser (6, 6a) in the direction of flow of the lower-boiling product mixture coming from the intermediate condenser.
10. Installation according to one of Claims 6, 7 or 8, characterized in that a separation column (14) for separating SiH_4 -containing product fractions from higher-boiling chlorosilane components is arranged downstream of the intermediate condenser (6a) in the direction of flow of the lower-boiling product mixture coming from the intermediate condenser.

11. Installation according to Claim 9 and 10, characterized in that the separation column (14) is arranged downstream of the rectifying section (7a).
- 5 12. Installation according to Claim 11, characterized in that a condenser (9a) is arranged between rectifying section (7a) and separation column (14).
13. Installation according to one of Claims 10 to 12, characterized in that the separation column (14) is operated at a pressure which is higher than that in
10 the intermediate condenser (6, 6a), and the product which is conducted to the separation column (14) is compressed.
14. Installation according to one of Claims 9 to 15, characterized in that a branch
15 line (25) which opens into the reactive/distillative reaction zone (2a) of the reaction column (1a) is connected to the bottom outlet (24) of the separation column (14).

Fig. 1

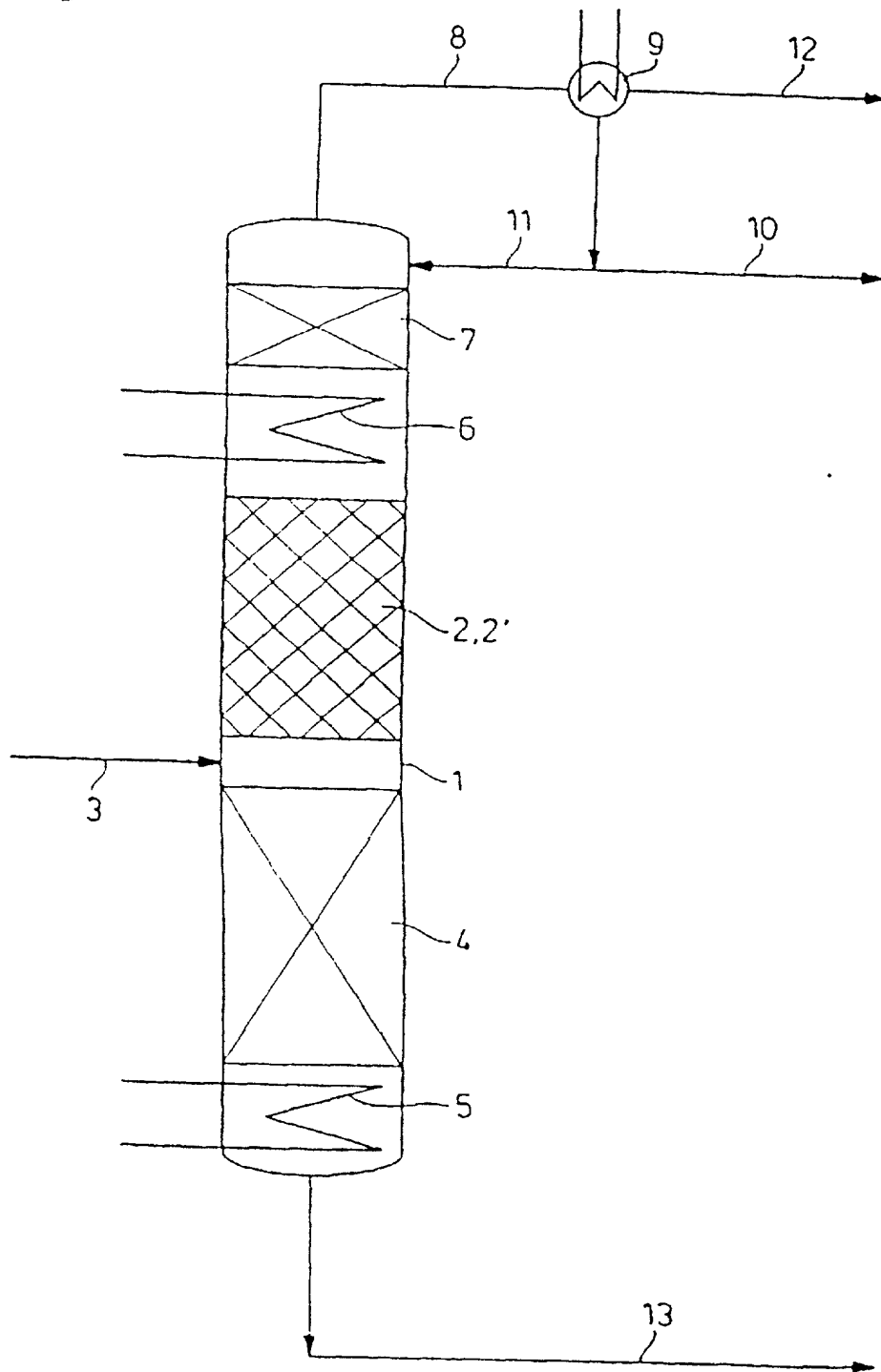


Fig. 2

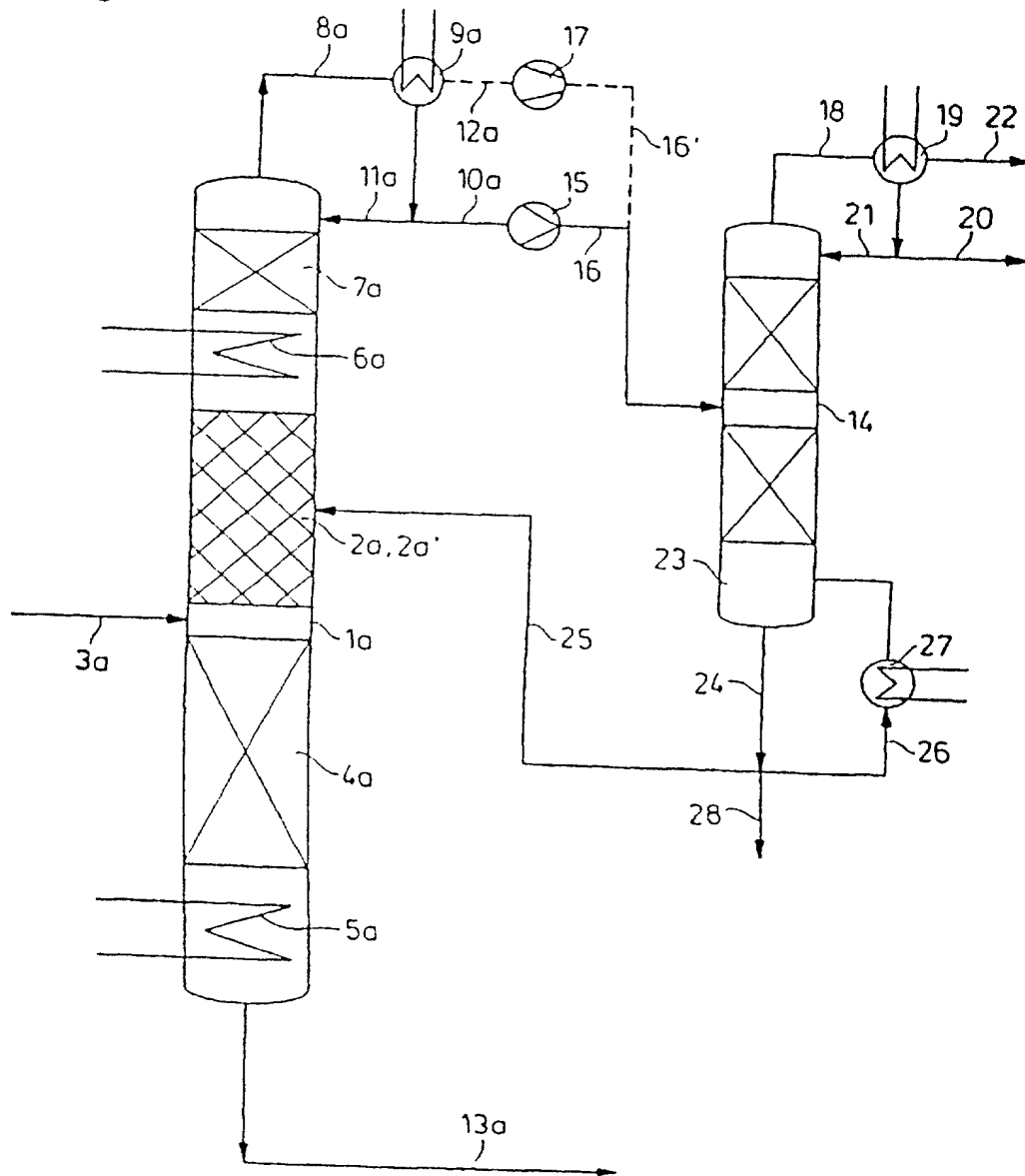
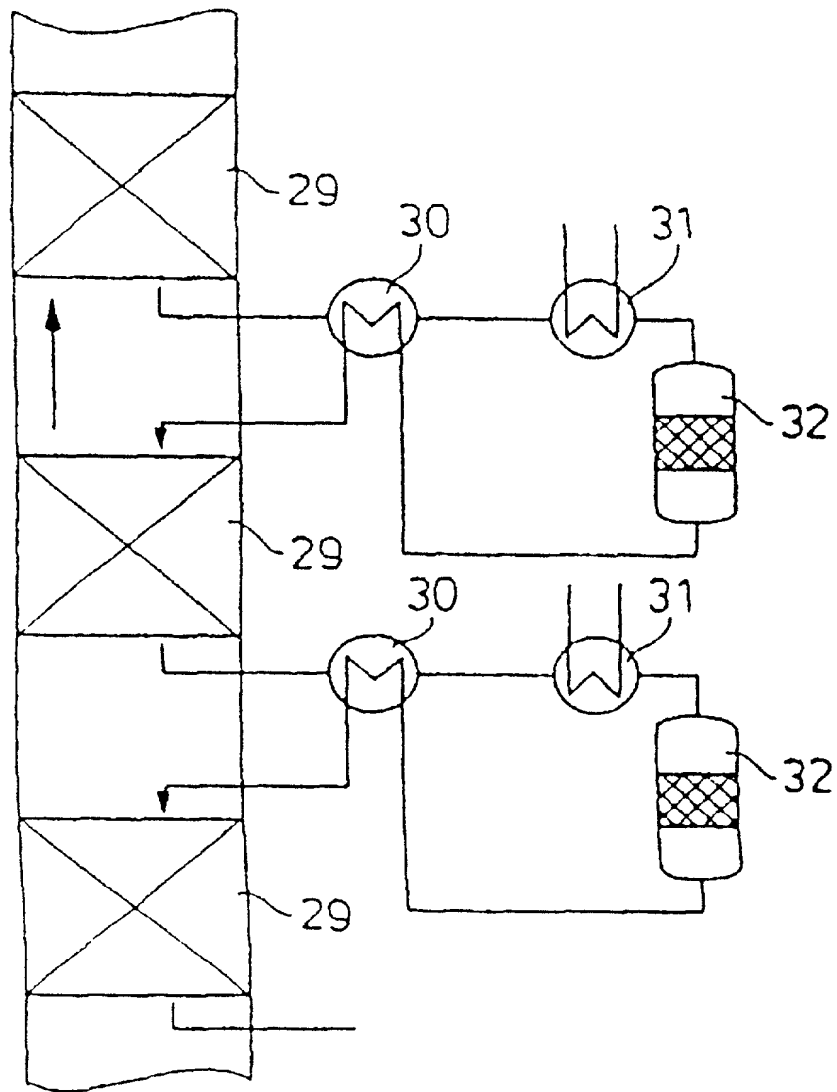


Fig. 3



As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

"METHOD AND SYSTEM FOR PRODUCING SILANE"

the specification of which is attached hereto,

or was filed on **December 14, 1999**

as a PCT Application Serial No. **PCT/EP99/09915**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

198 60 146.8
(Number)

Germany
(Country)

December 14, 1999
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

JOSEPH C. GIL, Patent Office Registration Number 26,602
ARON PREIS, Patent Office Registration Number 29,426
LYNDANNE M. WHALEN, Patent Office Registration Number 29,457
THOMAS W. ROY, Patent Office Registration Number 29,582
RICHARD E. L. HENDERSON, Patent Office Registration Number 31,619
GODFRIED R. AKORLI, Patent Office Registration Number 28,779
N. DENISE BROWN, Patent Office Registration Number 36,097
NOLAND J. CHEUNG, Patent Office Registration Number 39,138
DIDERICO VAN EYL, Patent Office Registration Number 38,641
CAROLYN M. SLOANE, Patent Office Registration Number 44,339
JAMES R. FRANKS, Patent Office Registration Number 42,552
JACKIE ANN ZURCHER, Patent Office Registration Number 42,251

all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

Send Correspondence To: <u>Patent Department</u> <u>Bayer Corporation</u> <u>100 Bayer Road</u> <u>Pittsburgh, Pennsylvania 15205-9741</u>	Direct Telephone Calls To: <u>(412) 777-2349</u>
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FULL NAME OF SOLE OR FIRST INVENTOR <u>Hans-Dieter Block</u>		INVENTOR'S SIGNATURE <u>Hans-Dieter Block</u>	DATE <u>9.5.2001</u>
RESIDENCE <u>D 51381 Leverkusen, Germany</u>		CITIZENSHIP <u>German</u>	
POST OFFICE ADDRESS <u>c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany</u>			
FULL NAME OF SECOND INVENTOR <u>Hans-Joachim Leimkühler</u>		INVENTOR'S SIGNATURE <u>Hans-Joachim Leimkühler</u>	DATE <u>1.5.2001</u>
RESIDENCE <u>D 51375 Leverkusen, Germany</u>		CITIZENSHIP <u>German</u>	
POST OFFICE ADDRESS <u>c/o Bayer Aktiengesellschaft, D 51358 Leverkusen, Germany</u>			
FULL NAME OF THIRD INVENTOR <u>Dirk Müller</u>		INVENTOR'S SIGNATURE <u>Dirk Müller</u>	DATE <u>08.05.2001</u>
RESIDENCE <u>D 51465 Bergisch Gladbach, Germany</u>		CITIZENSHIP <u>German</u>	
POST OFFICE ADDRESS <u>c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany</u>			
FULL NAME OF FOURTH INVENTOR <u>Johannes-Peter Schäfer</u>		INVENTOR'S SIGNATURE <u>Johannes-Peter Schäfer</u>	DATE <u>2001-05-08</u>
RESIDENCE <u>D 51515 Kürten, Germany</u>		CITIZENSHIP <u>German</u>	
POST OFFICE ADDRESS <u>c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany</u>			
FULL NAME OF FIFTH INVENTOR <u>Georg Ronge</u>		INVENTOR'S SIGNATURE <u>Georg Ronge</u>	DATE <u>2001-05-18</u>
RESIDENCE <u>D 40277 Düsseldorf, Germany</u>		CITIZENSHIP <u>German</u>	
POST OFFICE ADDRESS <u>c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany</u>			
FULL NAME OF SIXTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SEVENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			